

IN THE SPECIFICATION

Please amend page 1 by inserting the following heading between the title of the invention and the first paragraph:

“FIELD OF THE INVENTION”

Please amend page 1 by inserting the following heading between the first and second paragraphs:

“BACKGROUND OF THE INVENTION”

Please amend page 3 by inserting the following heading on line 3:

“BRIEF SUMMARY OF THE INVENTION”

Please amend page 7 by inserting the following heading on line 28:

“BRIEF DESCRIPTION OF THE DRAWINGS

Preferred features of the present invention...”

Please amend page 8 by inserting the following heading on line 11:

“DETAILED DESCRIPTION OF THE INVENTION

In the present invention, one can achieve...”

Please amend page 17 by inserting the following language between the “CLAIMS” heading and claim 1:

“I/We claim:”

Please amend page 3 by inserting the following text on line 8:

“Wet potentiometric titration procedures and cyclic voltammetry are frequently used to monitor the levels of known contaminant species in solutions. All of these processes take place in the liquid phase and use reversible electrode processes, mostly using water as the major constituent of the solvent and use electrons to directly effect oxidation/reduction. Gas phase electrochemistry is confined to the areas of electrochemical sensors, both potentiometric and amperometric, and solid oxide fuel cells neither of which use any kind of titration reaction.”

It will therefore be appreciated that, in contrast to the wet titrametric procedures of the prior art, the sensor of the present invention facilitates the titrametric determination of trace organic contaminants in the gaseous phase using a solid state electrolyte."

Please amend pages 7-8 by deleting the text on page 7 lines 6-32 through page 8 lines 1-23 as follows:

~~"In the absence of organic contaminants, at temperature T_{tit} and constant electrical current I_p , the potential difference across the cell, V_o , is constant and is determined by the equilibrium between the flux of oxygen anions (O^{2-}) arriving at the electrode surface and the rate of desorption of oxygen gas ($O_{2(g)}$) from the electrode surface according to equations 1 and 2 above.~~

~~However, when carbonaceous deposits are present on the electrode surface they are oxidised (combusted) to carbon dioxide by the flux of oxygen anions arriving at the electrode surface. This has the effect of reducing the equilibrium concentration of oxygen anions (O^{2-}) at the surface, which means that, in accordance with equation 3 above, the potential across the cell, V_{tit} , is increased relative to V_o . When the current I_p is applied to the cell, oxygen anions are forced to flow from the reference electrode to the measurement electrode where they react with the carbonaceous deposits formed at the surface thereof during the adsorption phase, which results in the formation of carbon dioxide. As the carbonaceous deposits are transformed into carbon dioxide their concentration progressively decreases to zero at the surface of the measurement electrode and the concentration of oxygen at the surface of the measurement electrode will increase to the constant equilibrium value determined by the flux of oxygen anions to the electrode. The potential difference across the cell then returns to the constant value, V_o , and provides an indication that all the carbonaceous deposits on the surface of the electrodes have been removed.~~

~~The total amount of carbonaceous deposit formed at the surface of the measurement electrode can be determined by measuring the total amount of oxygen transported to the measurement electrode by the application of current I_p (which is required to oxidise all of the carbonaceous deposits) over the time t_p taken for the potential difference across the cell to return from V_{tit} to V_o . Since the transport of each oxygen anion to the surface of the measurement electrode~~

~~requires the passage of two units of charge, the total quantity of oxygen atoms transported to the surface of the electrode is determined by the term:~~

$$\text{-----} I_p t_p / 2 \quad \text{Equation 7}$$

~~Since each atom of carbon deposited at the surface of the electrode requires two oxygen atoms for complete combustion, the total amount of carbon atoms oxidised during the titration phase and hence deposited at the electrode during the adsorption phase is:~~

$$\text{-----} I_p t_p / 4 \quad \text{Equation 8}$$

~~It will be appreciated that by controlling the time over which adsorption of the organic contaminants can occur on the surface of the measurement electrode, the value of the current I_p flowing between the reference and measurement electrodes at temperature T_{tit} and the time t_p taken for the potential difference across the cell to drop from V_{tit} to V_o , it is possible to titrimetrically monitor the levels of organic contaminants in the process environment in the parts per trillion (ppt) range or less. The sensor therefore provides a low cost alternative to the use of mass spectrometry and gas chromatography in the determination of low levels of organic impurities in process environments."~~

Please amend pages 9-14 by deleting the text on page 9 lines 1-24 and 29-30, page 10 lines 1-5, 10-11, 13-17 and 19-32, page 11 lines 1-32, page 12 lines 1-32, page 13 lines 1-32, and page 14 lines 1-4 as follows:

~~"The sensor is also easy to use and can be used at the point of use as well as the point of entry to provide accurate information about the process environments at all stages of the semiconductor fabrication process.~~

~~The total level of contaminants measured by the sensor can provide a semi-quantitative indication of the level of harmful organic contaminants present in the process environment. The non-contaminating light organic molecules present in the process environment do not stick to the surface of the measurement electrode and are not therefore measured. It is only the harmful organic contaminants, which have a high reaction probability with the electrode surface (and therefore with other surfaces encountered in the fabrication process) that undergo~~

~~dissociation and are therefore subsequently oxidised at the measurement electrode surface that are detected and therefore monitored by the measurement electrode.~~

~~Careful choice of the material applied to the measurement electrode or the material from which it is formed will cause some of the harmful organic contaminants to adsorb onto the surface of the measurement electrode in preference to others. Preferably the measurement electrode is formed from material whose uptake of organic material proceeds with a sticking probability of or about unity. In addition, the organic material is preferably efficiently adsorbed and cracked by the electrode material. Furthermore, the measurement electrode is suitably able to catalyse the dehydrogenation and cracking of organic contaminants. Suitable electrode materials include metals selected from the group comprising rhenium, osmium, iridium, ruthenium, rhodium, platinum and palladium and alloys thereof. Alloys of the aforementioned materials with silver, gold and copper may also be used.~~

~~The sensor is easily and readily manufactured using techniques known to a person skilled in the art. Sensing, reference and optionally counter electrodes can be applied to a thimble of an oxygen anion conductor solid state electrolyte such as yttria stabilised zirconia either in the form of an ink or a paint or using techniques such as sputtering. The sensing electrode is isolated from the reference and optional counter electrode via the formation of a gas tight seal. The sensor is suitably supplied with heater means to control the temperature of the electrolyte and means to monitor the voltage between the sensing electrode and the reference and counter electrodes respectively.~~

The reference electrode is suitably formed from a material that is able to catalyse the dissociation of oxygen in the reference environment, for example platinum. The reference environment can be derived from a gaseous or solid-state source of oxygen. Typically ~~atmospheric air is used as a gaseous reference source of oxygen although other gas compositions can be used.~~ Solid-state sources of oxygen typically comprise of a metal/metal oxide couple such as Cu/Cu₂O and Pd/PdO or a metal oxide/metal oxide couple such as Cu₂O/CuO. The particular solid state reference materials chosen will depend on the operating environment of the sensor and in particular the titration temperature T_{oit} . The solid state electrolyte comprising an oxygen anion conductor is suitably formed from a material that exhibits oxygen anion conduction at temperatures above 300°C. Suitable oxygen anion

conductors include gadolinium doped ceria and yttria stabilised zirconia. Preferred materials for use as the solid state oxygen anion conductor include 8% molar yttria stabilised zirconia (YSZ), which is commercially available.

A radiative heater may be used to control the temperature of the cell. Such heaters include heating filaments, wound around the solid state electrolyte. An electric light bulb can also be used. A thermocouple may be used to monitor the temperature of the cell.

Currents of between 100nA and 100pA may be used for driving oxygen anions between the reference and measurement electrodes. Currents outside this range can be used, depending upon the circumstances. The magnitude of the current used to drive the oxygen anions between the reference and measurement electrodes depends upon the surface area of the electrode and the amount of cracked hydrocarbon deposited at the surface thereof. Larger currents will generally be required for electrodes having a greater surface area or a large amount of cracked hydrocarbon deposited on the surface thereof. The sensor is preferably used in conjunction with a device for measuring the potential produced across the cell.

In use, the sensor continuously cycles between an adsorption mode and an oxygen titration mode:

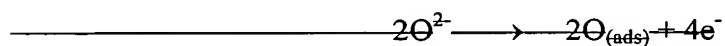
In the adsorption mode, the sensor is held at a constant temperature, T_{ads} , which is below the critical temperature, T_c , for oxygen anion conduction within the solid state electrolyte. The T_c for YSZ, for example, is in the range 300°C. T_{ads} and the sensing electrode material are chosen such that the catalytic properties of the sensing electrode, at T_{ads} , cause adsorbed organic material to de-hydrogenate/crack leading to the build up of carbonaceous deposits on the surface. For a platinum electrode, for example, T_{ads} is in the range 20 to 80°C. In the ideal case complete de-hydrogenation/cracking will occur leaving a surface layer of adsorbed carbon.

The sensor is held at temperature, T_{ads} , for a time, t_{ads} , during which adsorption of the organic contaminants occurs. The length of time, t_{ads} , is suitably between 10 and 105 seconds and is preferably of the order of 102-103 seconds. Greater sensitivities can be achieved using longer adsorption times. It is, however, desirable that saturation of the measurement electrode during

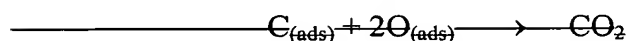
the adsorption phase is avoided as this will change the sticking/reaction probability of the surface, typically surface coverages of < 0.5 monolayers are desirable. In the event that saturation of the electrode occurs this can be overcome by burning the carbonaceous deposit off of the surface of the measurement electrode and re-adsorbing for a shorter period of time.

In the event that incomplete cracking of the hydrocarbon contaminant occurs during the adsorption phase, complete cracking can be achieved by raising the temperature of the sensor to a temperature intermediate that of the adsorption temperature, T_{ads} , and the titration temperature, T_{tit} , and optionally applying a potential V_i across the sensor, under which conditions complete cracking of the adsorbed hydrocarbon occurs. In some applications, V_i may be zero. The sensor is held at the intermediate temperature for a period of time sufficient to allow complete conversion of any uncracked hydrocarbon contaminant to a carbonaceous deposit on the surface of the measurement electrode.

In the oxygen titration mode, the sensor temperature is rapidly raised from either the adsorption temperature, T_{ads} , or the intermediate temperature to a fixed absolute temperature, T_{tit} , which is above T_o . During this temperature ramp de-hydrogenated organic material will remain on the surface. Once at T_{tit} , a small current I_p is forced to pass through the electrochemical cell, pumping oxygen to the sensing electrode surface, as per equation 9. Currents of the order of 100 nanoamps to 100 micro-amps are suitably used. The oxygen progressively combusts the carbonaceous residue on the sensing electrode in accordance with equation 10.



Equation 9



Equation 10

The potential of the sensing electrode, relative to the reference electrode, will tend to the equilibrium thermodynamic value predicted by the Nernst equation 3, as the titration reaction proceeds. When the equilibrium thermodynamic voltage V_o is reached the oxygen titration reaction is complete. The total amount of charge that has flowed through the cell during the titration reaction is directly proportional to the amount of oxygen reacted. For the ideal case the amount of carbon accumulated during the adsorption phase will be 1/4 of the total charge,

~~as per equations 9 and 10. The amount of carbon can be determined from the time taken in the adsorption phase and the surface area of the sensing electrode.~~

~~Wet potentiometric titration procedures and cyclic voltammetry are frequently used to monitor the levels of known contaminant species in solutions. All of these processes take place in the liquid phase and use reversible electrode processes, mostly using water as the major constituent of the solvent and use electrons to directly effect oxidation/reduction. Gas phase electrochemistry is confined to the areas of electrochemical sensors, both potentiometric and amperometric, and solid oxide fuel cells neither of which use any kind of titration reaction.~~

~~It will therefore be appreciated that, in contrast to the wet titrametric procedures of the prior art, the sensor facilitates the titrametric determination of trace organic contaminants in the gaseous phase using a solid state electrolyte.~~

~~Although the sensor can be used with just two electrodes (the reference and measurement electrode) only, it is preferred to use an electrode arrangement comprising a counter electrode in addition to the measurement and reference electrodes as described above. The counter electrode is positioned adjacent to the reference electrode and in contact with the same reference environment as the reference electrode. In this preferred embodiment, the current I_p flows between the counter electrode and the measurement electrode. The reference electrode therefore provides a constant reference environment from which the electrochemical potentials of both the measurement and counter electrodes and therefore the potential difference across the cell can be determined. The counter electrode is preferably formed from a material, such as platinum, which catalyses the dissociation of oxygen.~~

~~The dimensions of the top and bottom surfaces of the sensor are typically of the order of a few square centimetres or less. The electrodes formed or deposited on each of the surfaces are therefore dimensioned accordingly. The sensing and counter electrodes are each typically of the order of 1 cm^2 . The reference electrode is usually of a lesser dimension. The electrodes are typically from about 0.1 to about 50um in thickness.~~

~~It will be appreciated that the sensor can be used to monitor the levels of trace organic contaminants in process environments, and so a second aspect of the invention provides the~~

~~use of a sensor as aforementioned to monitor levels of trace organic contaminants in process environments.”~~

Please amend pages 15-16 as follows:

“A reference electrode 16 is formed on the opposite surface of the electrolyte 12 to the measurement electrode 10 using similar techniques to those described above for measurement electrode 10. In the preferred embodiment, the reference electrode 16 is formed from platinum. Alternatively, the reference electrode 16 may be formed from any other material that is able to catalyse the dissociation of oxygen to oxygen anions. In use, the reference electrode 16 is placed in contact with a reference environment 18, which, in this embodiment, is a gaseous source of oxygen at constant pressure such as atmospheric air. Typically atmospheric air is used as a gaseous reference source of oxygen although other gas compositions can be used. The electrodes 10,16 and the electrolyte 12 together form an electrochemical cell 1413.”

Please amend page 16 by inserting the following text on line 9 as follows:

“A radiative heater may be used to control the temperature of the cell. Such heaters include heating filaments, wound around the solid state electrolyte. An electric light bulb can also be used. A thermocouple may be used to monitor the temperature of the cell.”

Please amend page 16 line 10 as follows:

“The sensor of Fig. 1 is provided with a heater and thermocouple...”

Please amend page 16 by inserting the following text on line 22 as follows:

“Currents of between 100nA and 100pA may be used for driving oxygen anions between the reference and measurement electrodes. Currents outside this range can be used, depending upon the circumstances. The magnitude of the current used to drive the oxygen anions between the reference and measurement electrodes depends upon the surface area of the electrode and the amount of cracked hydrocarbon deposited at the surface thereof. Larger currents will generally be required for electrodes having a greater surface area or a large amount of cracked hydrocarbon deposited on the surface thereof. The sensor is preferably used in conjunction with a device for measuring the potential produced across the cell.

In use, the sensor continuously cycles between an adsorption mode and an oxygen titration mode:

In the adsorption mode, the sensor is held at a constant temperature, T_{ads} , which is below the critical temperature, T_c , for oxygen anion conduction within the solid state electrolyte. The T_c for YSZ, for example, is in the range 300°C. T_{ads} and the sensing electrode material are chosen such that the catalytic properties of the sensing electrode, at T_{ads} , cause adsorbed organic material to de-hydrogenate/crack leading to the build up of carbonaceous deposits on the surface. For a platinum electrode, for example, T_{ads} is in the range 20 to 80°C. In the ideal case complete de-hydrogenation/cracking will occur leaving a surface layer of adsorbed carbon.

The sensor is held at temperature, T_{ads} , for a time, t_{ads} , during which adsorption of the organic contaminants occurs. The length of time, t_{ads} , is suitably between 10 and 105 seconds and is preferably of the order of 102-103 seconds. Greater sensitivities can be achieved using longer adsorption times. It is, however, desirable that saturation of the measurement electrode during the adsorption phase is avoided as this will change the sticking/reaction probability of the surface, typically surface coverages of < 0.5 monolayers are desirable. In the event that saturation of the electrode occurs this can be overcome by burning the carbonaceous deposit off of the surface of the measurement electrode and re- adsorbing for a shorter period of time.

In the event that incomplete cracking of the hydrocarbon contaminant occurs during the adsorption phase, complete cracking can be achieved by raising the temperature of the sensor to a temperature intermediate that of the adsorption temperature, T_{ads} , and the titration temperature, T_{tit} , and optionally applying a potential V_i across the sensor, under which conditions complete cracking of the adsorbed hydrocarbon occurs. In some applications, V_i may be zero. The sensor is held at the intermediate temperature for a period of time sufficient to allow complete conversion of any uncracked hydrocarbon contaminant to a carbonaceous deposit on the surface of the measurement electrode.”

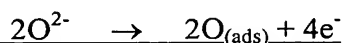
Please amend page 16 lines 23-25 as follows:

“In use, the sensor of Fig. 1 is cycled between an adsorption phase and a titration phase. In the adsorption phase, the measurement electrode 10 is exposed to an environment to

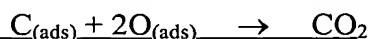
be monitored, including any organic contaminants. ~~The~~ As discussed above, the sensor is held at a temperature T_{ads} for a time t_{ads} during which..."

Please amend page 17 by inserting the following text on line 5 as follows:

"In the oxygen titration mode, the sensor temperature is rapidly raised from either the adsorption temperature, T_{ads} , or the intermediate temperature to a fixed absolute temperature, T_{tit} , which is above T_0 . During this temperature ramp de-hydrogenated organic material will remain on the surface. Once at T_{tit} , a small current I_p is forced to pass through the electrochemical cell, pumping oxygen to the sensing electrode surface, as per equation 7. Currents of the order of 100 nanoamps to 100 micro-amps are suitably used. The oxygen progressively combusts the carbonaceous residue on the sensing electrode in accordance with equation 8.



Equation 7



Equation 8

The potential of the sensing electrode, relative to the reference electrode, will tend to the equilibrium thermodynamic value predicted by the Nernst equation 3, as the titration reaction proceeds. When the equilibrium thermodynamic voltage V_0 is reached the oxygen titration reaction is complete. The total amount of charge that has flowed through the cell during the titration reaction is directly proportional to the amount of oxygen reacted. For the ideal case the amount of carbon accumulated during the adsorption phase will be 1/4 of the total charge, as per equations 7 and 8. The amount of carbon can be determined from the time taken in the adsorption phase and the surface area of the sensing electrode.

The total amount of carbonaceous deposit formed at the surface of the measurement electrode can be determined by measuring the total amount of oxygen transported to the measurement electrode by the application of current I_p (which is required to oxidise all of the carbonaceous deposits) over the time t_p taken for the potential difference across the cell to return from V_{tit} to V_0 . Since the transport of each oxygen anion to the surface of the measurement electrode requires the passage of two units of charge, the total quantity of oxygen atoms transported to the surface of the electrode is determined by the term:

$$I_p t_p / 2$$

Equation 9

Since each atom of carbon deposited at the surface of the electrode requires two oxygen atoms for complete combustion, the total amount of carbon atoms oxidised during the titration phase and hence deposited at the electrode during the adsorption phase is:

$$I_p t_p / 4$$

Equation 10

”

Please further amend page 17 by inserting the following text beginning on line 8 as follows:

“During the titration phase the potential difference across the cell is monitored, together with the time taken for the potential difference to reach a constant value, V_o , characterised by the current I_p . In the absence of organic contaminants, at temperature T_{tit} and constant electrical current I_p , the potential difference across the cell, V_o , is constant and is determined by the equilibrium between the flux of oxygen anions (O^{2-}) arriving at the electrode surface and the rate of desorption of oxygen gas ($O_{2(g)}$) from the electrode surface according to equations 1 and 2 above.

However, when carbonaceous deposits are present on the electrode surface they are oxidised (combusted) to carbon dioxide by the flux of oxygen anions arriving at the electrode surface. This has the effect of reducing the equilibrium concentration of oxygen anions (O^{2-}) at the surface, which means that, in accordance with equation 3 above, the potential across the cell, V_{tit} , is increased relative to V_o . When the current I_p is applied to the cell, oxygen anions are forced to flow from the reference electrode to the measurement electrode where they react with the carbonaceous deposits formed at the surface thereof during the adsorption phase, which results in the formation of carbon dioxide. As the carbonaceous deposits are transformed into carbon dioxide their concentration progressively decreases to zero at the surface of the measurement electrode and the concentration of oxygen at the surface of the measurement electrode will increase to the constant equilibrium value determined by the flux of oxygen anions to the electrode. The potential difference across the cell then returns to the constant value, V_o , and provides an indication that all the carbonaceous deposits on the surface of the electrodes have been removed.

The establishment of this constant potential indicates that sufficient oxygen has passed between the reference and measurement electrodes to cause complete oxidation of all of the carbonaceous deposits present at the surface of the measurement electrode 10 and therefore that the end point of the oxidative titration has been reached.”

Please further amend page 17 by inserting the following text on line 21 as follows:

“It will be appreciated that by controlling the time over which adsorption of the organic contaminants can occur on the surface of the measurement electrode, the value of the current I_p flowing between the reference and measurement electrodes at temperature T_{tit} and the time t_p taken for the potential difference across the cell to drop from V_{tit} to V_o , it is possible to titrimetrically monitor the levels of organic contaminants in the process environment in the parts per trillion (ppt) range or less. The sensor therefore provides a low cost alternative to the use of mass spectrometry and gas chromatography in the determination of low levels of organic impurities in process environments.

Although the sensor can be used with just two electrodes (the reference and measurement electrode) only, it is preferred to use an electrode arrangement comprising a counter electrode in addition to the measurement and reference electrodes as described above. The counter electrode is positioned adjacent to the reference electrode and in contact with the same reference environment as the reference electrode. In this preferred embodiment, the current I_p flows between the counter electrode and the measurement electrode. The reference electrode therefore provides a constant reference environment from which the electrochemical potentials of both the measurement and counter electrodes and therefore the potential difference across the cell can be determined. The counter electrode is preferably formed from a material, such as platinum, which catalyses the dissociation of oxygen.”

Please amend page 18 by inserting the following text on line 3 as follows:

“Sensing, reference and optionally counter electrodes can be applied to a thimble of an oxygen anion conductor solid state electrolyte such as yttria stabilised zirconia either in the form of an ink or a paint or using techniques such as sputtering. The sensing electrode is isolated from the reference and optional counter electrode via the formation of a gas tight seal. The sensor is suitably supplied with heater means to control the temperature of the electrolyte

and means to monitor the voltage between the sensing electrode and the reference and counter electrodes respectively.

The sensor is also easy to use and can be used at the point of use as well as the point of entry to provide accurate information about the process environments at all stages of the semiconductor fabrication process. The sensor is easily and readily manufactured using techniques known to a person skilled in the art.

The total level of contaminants measured by the sensor can provide a semi- quantitative indication of the level of harmful organic contaminants present in the process environment. The non-contaminating light organic molecules present in the process environment do not stick to the surface of the measurement electrode and are not therefore measured. It is only the harmful organic contaminants, which have a high reaction probability with the electrode surface (and therefore with other surfaces encountered in the fabrication process) that undergo dissociation and are therefore subsequently oxidised at the measurement electrode surface that are detected and therefore monitored by the measurement electrode.

Careful choice of the material applied to the measurement electrode or the material from which it is formed will cause some of the harmful organic contaminants to adsorb onto the surface of the measurement electrode in preference to others. Preferably the measurement electrode is formed from material whose uptake of organic material proceeds with a sticking probability of or about unity. In addition, the organic material is preferably efficiently adsorbed and cracked by the electrode material. Furthermore, the measurement electrode is suitably able to catalyse the dehydrogenation and cracking of organic contaminants.

Solid-state sources of oxygen typically comprise of a metal/metal oxide couple such as Cu/Cu₂O and Pd/PdO or a metal oxide/metal oxide couple such as Cu₂O/CuO. The particular solid-state reference materials chosen will depend on the operating environment of the sensor and in particular the titration temperature T_{tit} . The solid state electrolyte comprising an oxygen anion conductor is suitably formed from a material that exhibits oxygen anion conduction at temperatures above 300°C.

The dimensions of the top and bottom surfaces of the sensor are typically of the order of a few square centimetres or less. The electrodes formed or deposited on each of the surfaces are therefore dimensioned accordingly. The sensing and counter electrodes are each typically of the order of 1 cm². The reference electrode is usually of a lesser dimension. The electrodes are typically from about 0.1 to about 50um in thickness.

It will be appreciated that the sensor can be used to monitor the levels of trace organic contaminants in process environments, and so a second aspect of the invention provides the use of a sensor as aforementioned to monitor levels of trace organic contaminants in process environments.”